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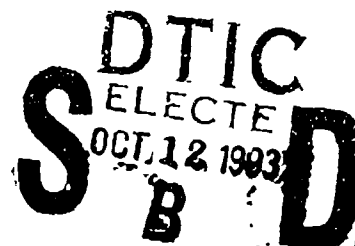
GAP Analyses: NMR Methods

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FOREWORD

Glycidyl azide polymer (GAP) and GAP azide are an energetic binder and plasticizer system targeted for use in advanced propulsion formulations. This report describes several nuclear magnetic resonance (NMR) techniques used to characterize several lots of GAP and GAP azide. Polymer molecular weights and equivalent weights are accessible by these methods.

This report has been reviewed for technical accuracy by Geoffrey A. Lindsay.

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22 September 1993

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13. ABSTRACT (Maximum 200 words) (U) Glycidyl azide polymer (GAP) is under investigation as an energetic binder for several military applications. Hydroxy terminated GAP, where two, three, or four end groups per molecule are present has been studied for use in urethane cured formulations. A key to understanding the cure behavior in these systems is an accurate measure of hydroxy equivalent weight. NMR investigations of equivalent weights have been undertaken in our laboratory and we will briefly describe the results for several GAP lots available to us. NMR is quite sensitive to the initiator present and we can easily distinguish butane diol or trimethylol propane initiated systems. In addition, the carbon-13 NMR spectra of GAP samples were studied in detail allowing for assignment of all relevant resonances due to main chain and terminal groups. Samples of GAP azide, a moderate molecular weight plasticizer, were also studied. This material was found to contain small levels of hydroxy functionality, on the order of one per 10,000 glycidyl groups, however, it was also clear that methylene chloride solvent remains behind even after solvent stripping and chromatographic separation. This made the analysis of hydroxy equivalent weight difficult because of coincidental overlap of these resonances.					
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INTRODUCTION

Difunctional and trifunctional hydroxy terminated gap azide polymer (GAP) are promising candidates for several advanced propellant formulations. The advent of GAP azide as a moderate molecular weight plasticizer will certainly improve the performance in these systems. A primary goal of this present work was to study in detail the structure of several candidate lots of GAP and GAP azide. Our goal was to identify the major structures present and to look for some of the minor contaminants present in these materials.

EXPERIMENTAL SECTION

Samples of GAP or GAP azide were dissolved in chloroform-d solvent. Trifluoroacetic anhydride (TFAA) was added in order to acetylate the polymer end groups. Since hydroxy equivalent weights were expected to be important features in both the GAP and GAP azide samples, this procedure was performed on both. The terminal methine resonance is expected to shift down field by approximately 1 part per million (ppm) upon trifluoroacetylation and indeed a resonance centered at 5.26 ppm is indicative of the terminal methine functional group (the group that was initially an alcohol functional group). Simple integration of this resonance and comparison to the bulk polymer resonances found between 4 and 3 ppm yields a measure of polymer equivalent weight when the corresponding numbers of protons contributing to each signal are compared. GAP azide samples treated with TFAA often exhibited a comparable signal near 5.2, however the relative integral of this signal as compared to the main chain resonance was diminished considerably as expected for the GAP azide structure. Carbon-13 NMR and inverse detected proton-carbon correlated spectra of GAP and GAP azide samples were used for peak assignments and structure confirmation. In addition, an attached proton test (distortionless enhancement by polarization transfer (DEPT)) was used to distinguish methine from methylene carbon resonances. The DEPT experiment was especially useful in identifying the terminal alcohol functional groups in GAP as secondary alcohols.

RESULTS AND DISCUSSION

Several samples of GAP have been analyzed in detail. These samples are lots 1000-1-2, 50-1, 50-2, and 50-3-XL. An in-depth analysis of the nuclear magnetic resonance (NMR) data on GAP 1000-1-2 will be presented and then a brief summary of results for the other three samples will follow. Note that our results indicate that lot 1000-1-2 is a trimethylolpropane (TMP) initiated polymer, hence a triol, whereas, 50-1, 50-2, and 50-3-XL are most likely initiated with an aliphatic polyol perhaps ethanediol in combination with butanediol or pentacrythritol. We are not likely to observe this in the proton NMR but perhaps extensive carbon-13 and proton/carbon correlated studies will help us to identify specific initiators.

NMR ANALYSIS OF GAP LOT 1000-1-2

Proton NMR of GAP lot 1000-1-2 in chloroform-d clearly show the ethyl group of TMP at 0.82 and 1.34 ppm (see Figure 1). This information alone can be used to estimate this system's molecular weight; however, addition of TFSA (see Figure 2) leads to the appearance of a resonance at 5.23 ppm which we assign to the trifluoroacetylated terminal methine unit of the polymer. It is then a simple matter to calculate the average number of monomer units per chain, add on the initiator molecular weight, and end up with a NMR molecular weight of 3600. Of course, this assumes a functionality of 3 as required for TMP initiator and thus we generate an equivalent weight of 1200 per hydroxy unit.

Carbon-13 NMR spectra are displayed in Figures 3-5. Figures 3 and 4 demonstrate the effect of added TFSA, which leads to the appearance of a new resonance at 75.2 ppm and Figure 5, a DEPT experiment where methines point down and methylene carbons point up clearly demonstrates that the terminal residue is indeed a methine carbon; hence, the alcohol functionality in this sample is most assuredly a secondary alcohol. One last type of experiment as depicted in Figures 6 and 7 is a proton/carbon correlated experiment. This two dimensional approach allows us to identify which proton resonances are associated with which carbon resonances. Figure 7 shows a region of the 2-d data set which depict the terminal methine residue having a proton chemical shift of 5.2 and a carbon chemical shift of 75.2 ppm. The NMR data for this GAP lot are quite consistent with a functionality = 3 system and a molecular weight of 3600 or 1200 per hydroxy unit.

ANALYSIS OF GAPS 50-1, 50-2, AND 50-3-X

The NMR molecular weights for these lots of GAP were also measured by analysis of TFSA treated samples. A resonance at 5.23 ppm is once again indicative of methine terminated polymer chains. Sample 50-1 has a calculated NMR molecular weight of 2360 if the functionality is presumed to be 2. In any event the hydroxy equivalent weight would be 1180 (see Figure 8). Similarly, lot 50-2 has a calculated molecular weight of 2380 and an equivalent weight of 1190 (Figure 9). Sample 50-3-XL (Figure 10) has a slightly higher molecular weight of 5760 if F is equal to 4 or 1440 per hydroxyl functionality. Carbon-13 analysis of these samples were consistent with the structures as described above.

ANALYSIS OF GAP POLYOL SAMPLE L-12369 AND A SECOND GAP SAMPLE TETRAOL 50-3-XL

Two additional samples were studied by proton NMR only. The resulting molecular weight for polymer L-12369, assuming a functionality of 2.75, would be 5104 and the equivalent weight would be 1856. The last GAP to be analyzed is probably a repeat of GAP 50-3-XL. It was delivered separately and contains the lot designation 50-3-XL, but it also carries the tetraol designation thus being labeled GAP tetraol 50-3-XL. We can perhaps assume the initiator is pentaerythritol for this sample. Our calculation of equivalent weight is quite consistent with our previous determination yielding a calculated equivalent weight of 1406 and a molecular weight of 5624 if the functionality is assumed to be 4.

ANALYSIS OF GAP AZIDES

Several samples of GAP azides were also analyzed by NMR techniques. They were all labeled Lot 200-2; however, the further treatment included stripping solvent and some form of chromatographic separation where first and last fractions were obtained. One major observation was that residual methylene chloride solvent is not completely removed by the stripping techniques employed. This does hinder the equivalent weight analysis since the solvent peak is close to the trifluoroacetylated terminal methine resonance. However, we do observe a small amount of trifluoroacetylated methine as shown in Figure 11. Based on this resonance being assigned to a trifluoroacetylated methine we can conclude that there are 9500 glycidylazide units per hydroxy functionality or an equivalent weight of 940,500. Chromatography does seem to remove most of the residual solvent as demonstrated in Figures 12 and 13 for the first and last chromatographic fractions and our calculated functionality for both of these fractions appears to decline to 579,000 and 535,000 for the first and last fractions, respectively. In all GAP azide samples there is a small amount of an aromatic impurity detected in the proton NMR spectra. Without a better idea of the source or identity of this impurity we can only guess that it is present at 0.01 to 0.1%. A similar amount of an aliphatic hydrocarbon is also present.

SUMMARY

NMR analysis of GAP and GAP azides offers many advantages over conventional equivalent weight analysis. Sample preparation is minimal, and the results are easily interpretable in terms of equivalent weights and gross structural features. In-depth analysis by carbon and 2-dimensional NMR will allow direct observation of terminal functionalities and initiator groups. Our results to date are given in Table 1.

TABLE 1. GAP and GAP Azide NMR Equivalent Weights.

GAP sample	Equivalent weight	Functionality
1000-1-2	1,200	3.0
50-1	1,180	2.0
50-2	1,190	2.0
50-3-XL	1,440	4.0
L-12369	1,856	2.75
Tetraol (50-3-XL)	1,406	4.0
Azide 200-2 (stripped)	940,500	0.0
Azide 200-2 (first)	579,000	0.0
Azide 200-2 (last)	535,000	0.0

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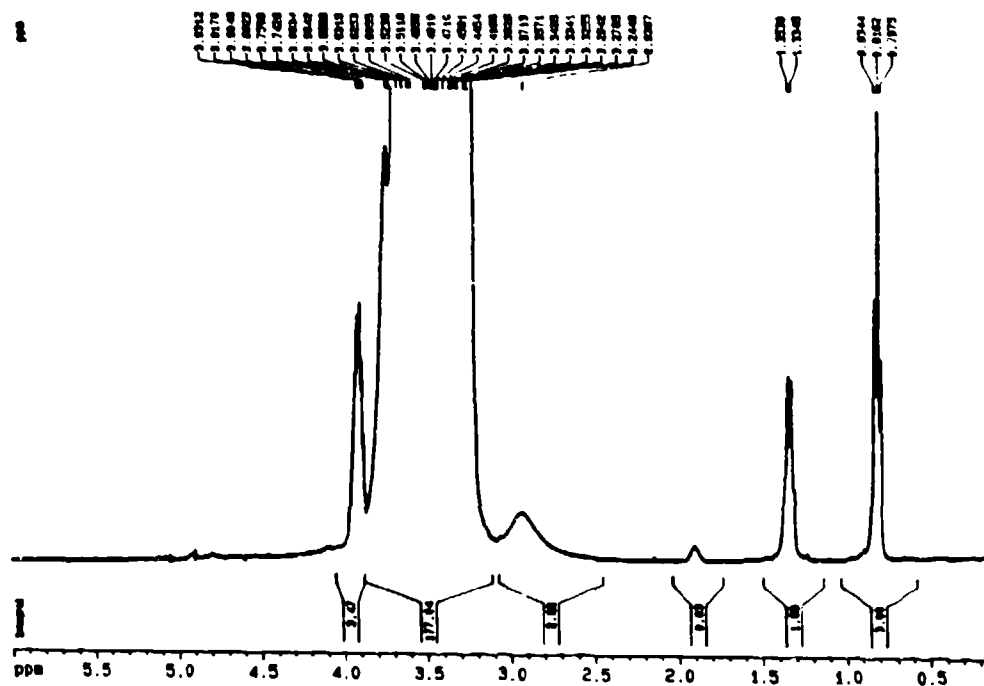


FIGURE 1. 400 MHz ¹H NMR Spectrum of GAP 1000-1-2 in CDCl₃ Solvent.

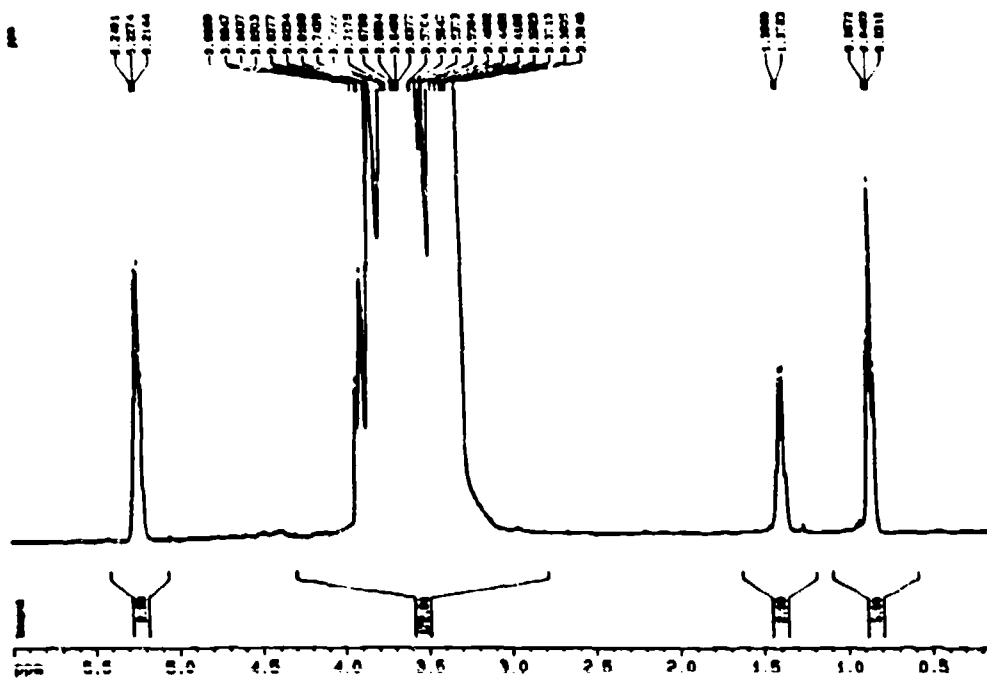


FIGURE 2. 400 MHz ¹H NMR Spectrum of GAP 1000-1-2 in CDCl₃ With Excess Trifluoroaceticanhydride (TFAA) Added.

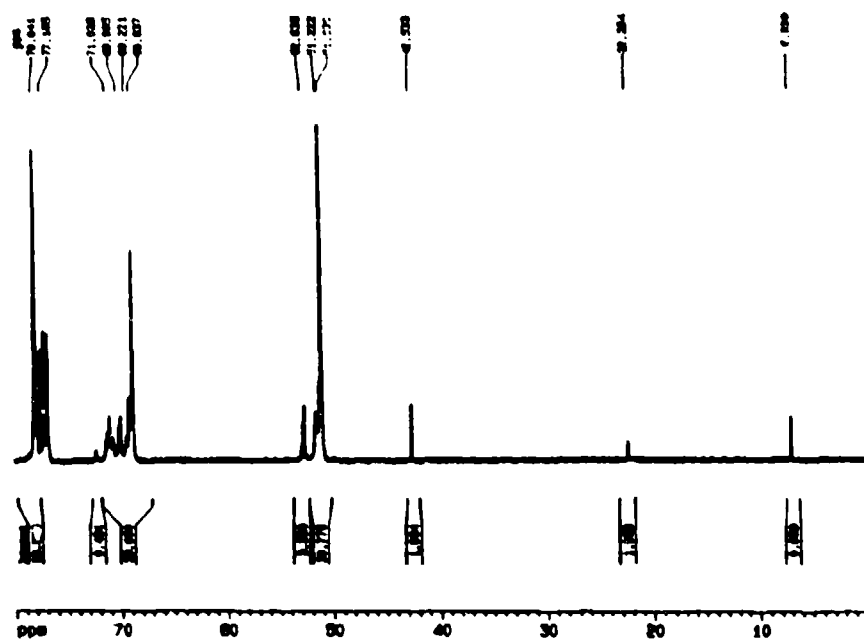


FIGURE 3. 100 MHz ^1H Decoupled ^{13}C NMR Spectrum of GAP 1000-1-2.

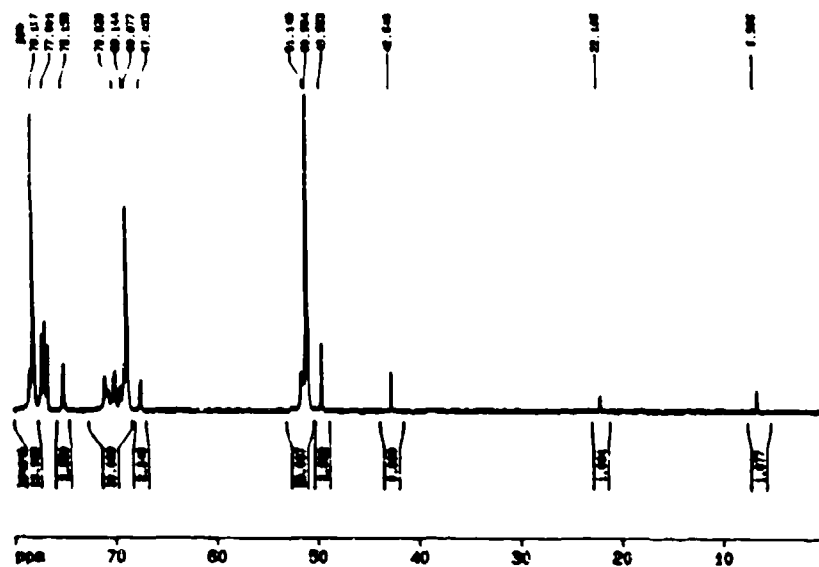


FIGURE 4. 100 MHz ^1H Decoupled ^{13}C NMR Spectrum of GAP 1000-1-2 With Excess TFAA Added.

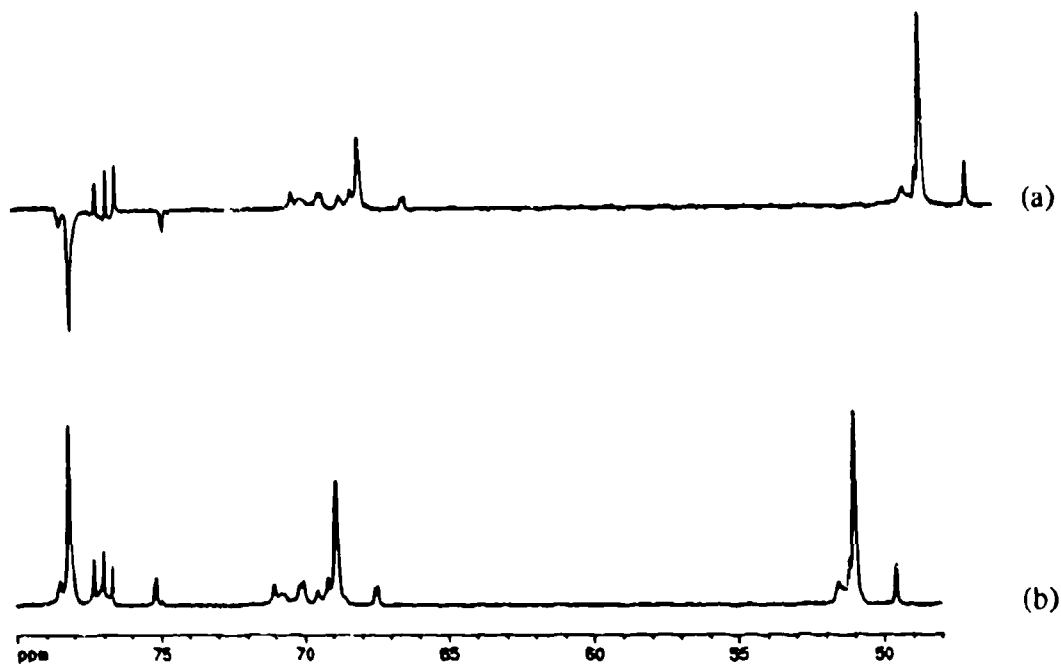


FIGURE 5. (a) Gated Spin Echo (GASPE) ^{13}C NMR With CH₂ up and CH Down of GAP 1000-1-2 and (b) ^{13}C Spectrum of GAP 1000-1-2.

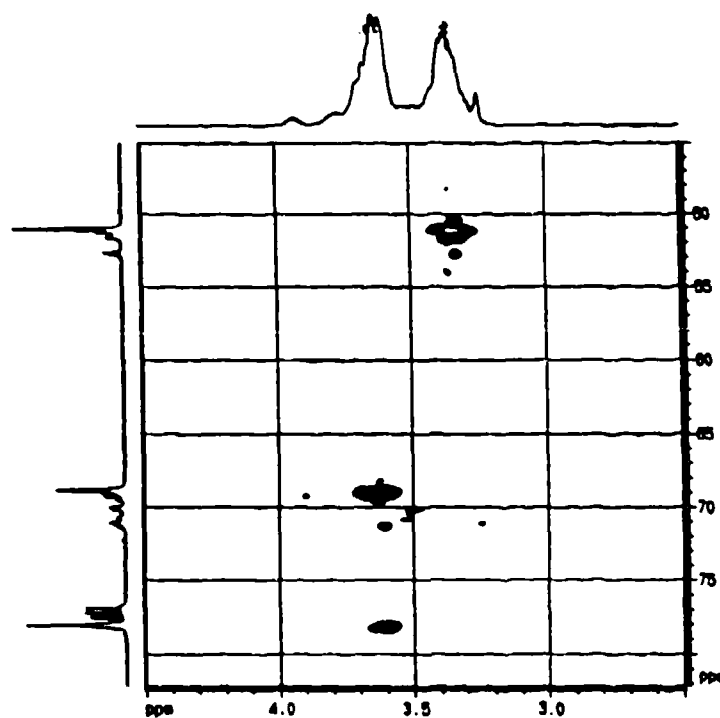


FIGURE 6. Heteronuclear Multiple Quantum Coherence (HMQC) Displaying Short Range $^1\text{H}/^{13}\text{C}$ Correlations of GAP 1000-1-2.

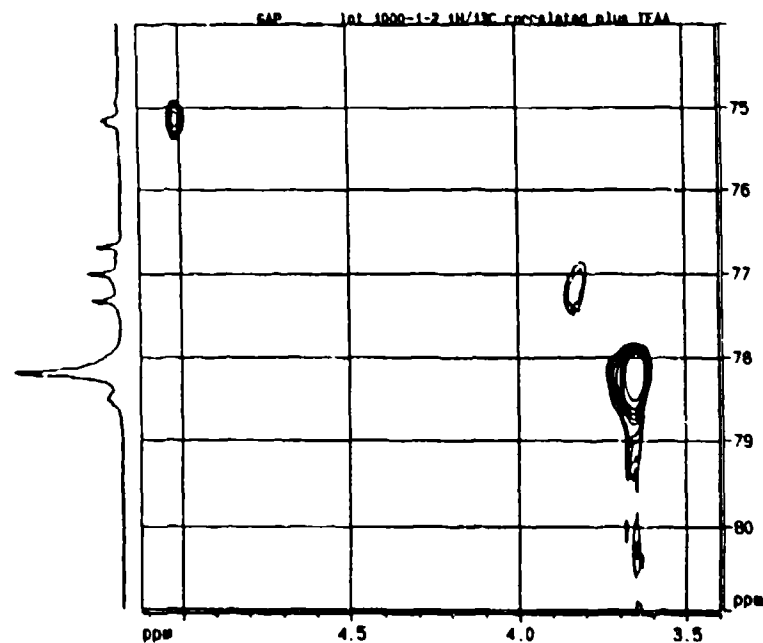


FIGURE 7. HMQC Spectrum of GAP 1000-1-2 Plus Excess TFAA.

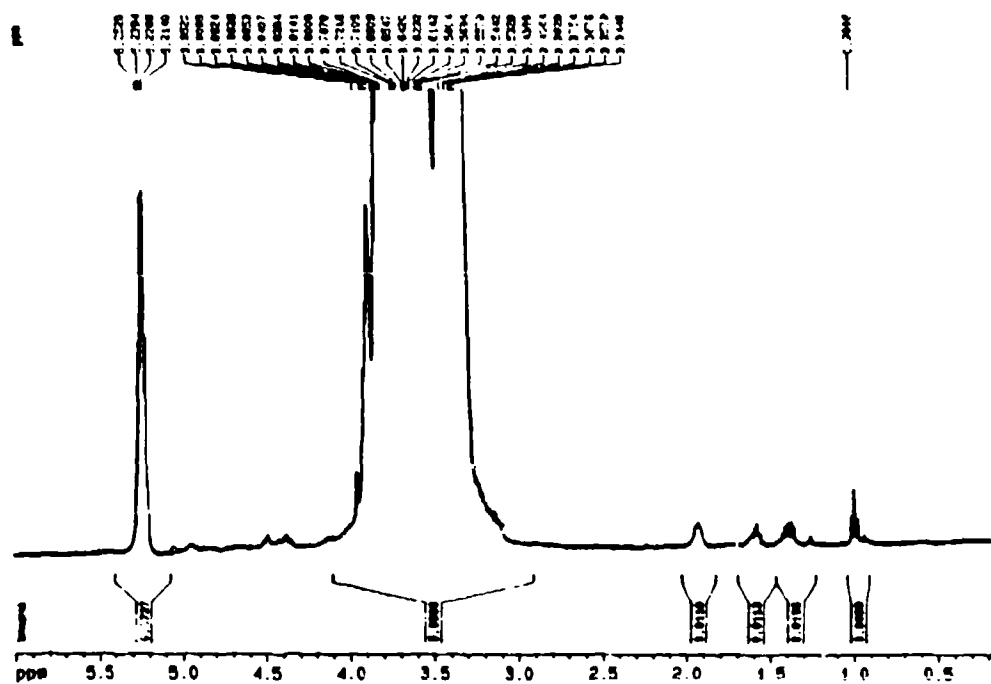


FIGURE 8. 400 MHz ^1H NMR Spectrum of GAP 50-1 Plus Excess TFAA.

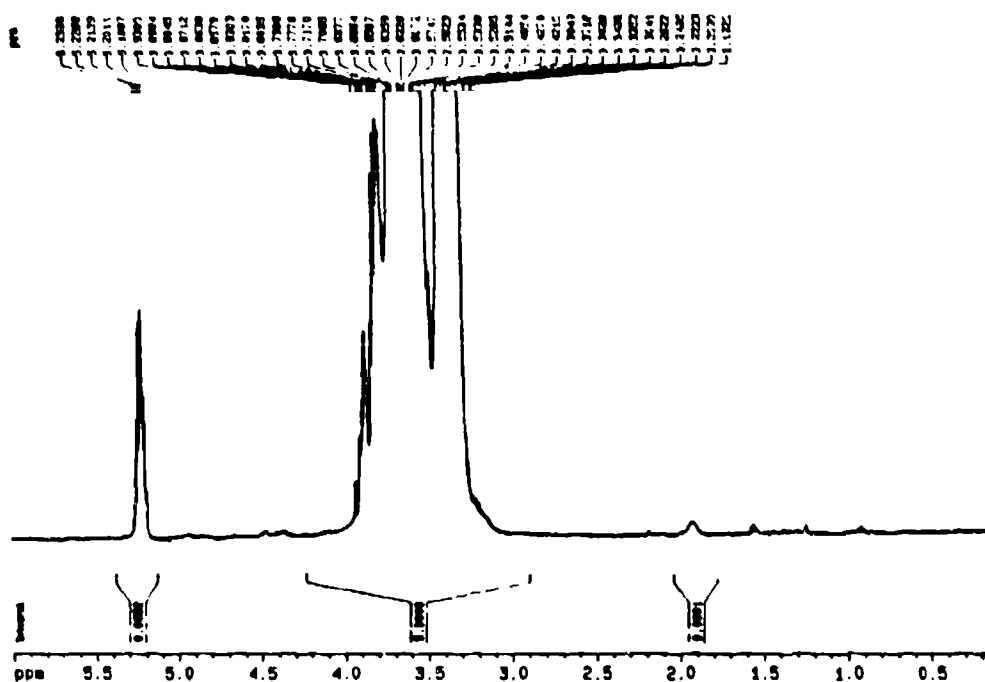


FIGURE 9. 400 MHz ^1H NMR Spectrum of GAP 50-2 Plus Excess TFAA.

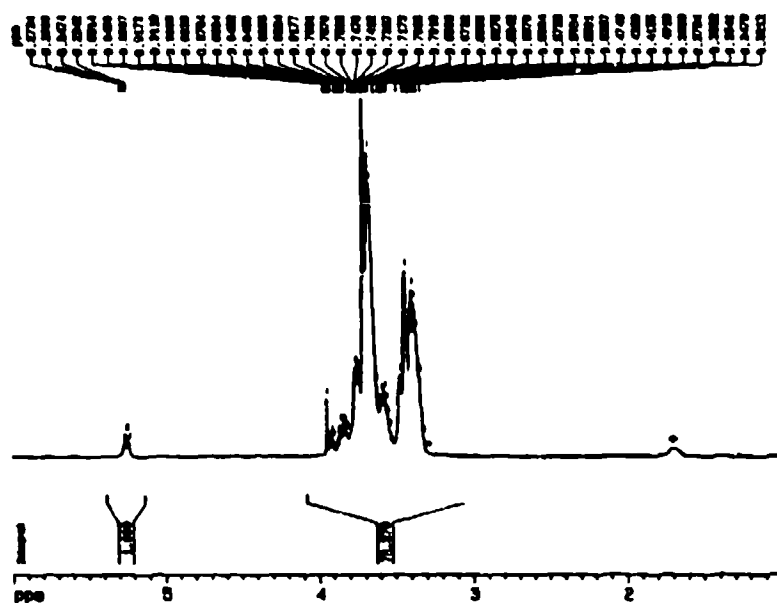


FIGURE 10. 400 MHz ^1H NMR Spectrum of GAP 50-3-XL Plus Excess TFAA.

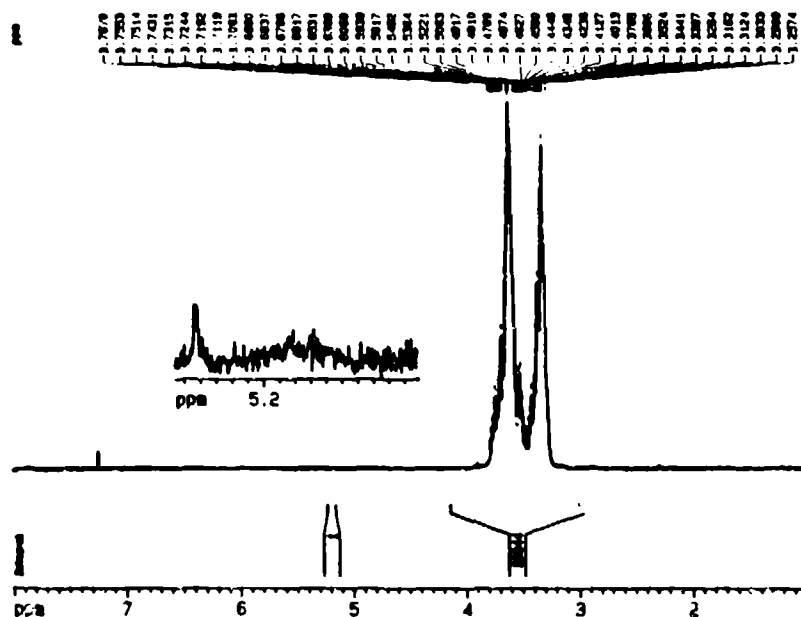


FIGURE 11. 400 MHz ^1H NMR Spectrum of GAP Azide—200 After Chromatography, Plus Excess TFSA. Inset: expanded region.

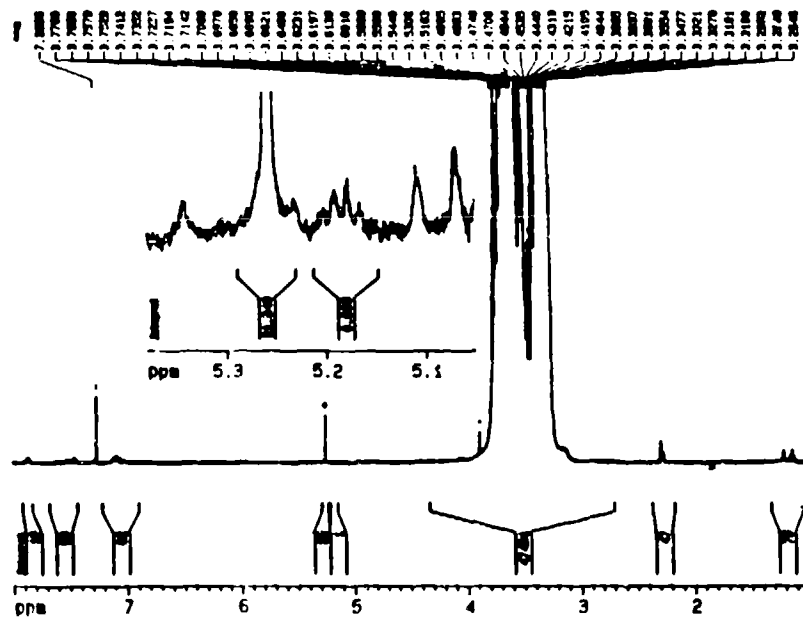


FIGURE 12. 400 MHz ^1H NMR Spectrum of GAP Azide Lot 200-2, Plus Excess TFSA. Inset: expanded region.

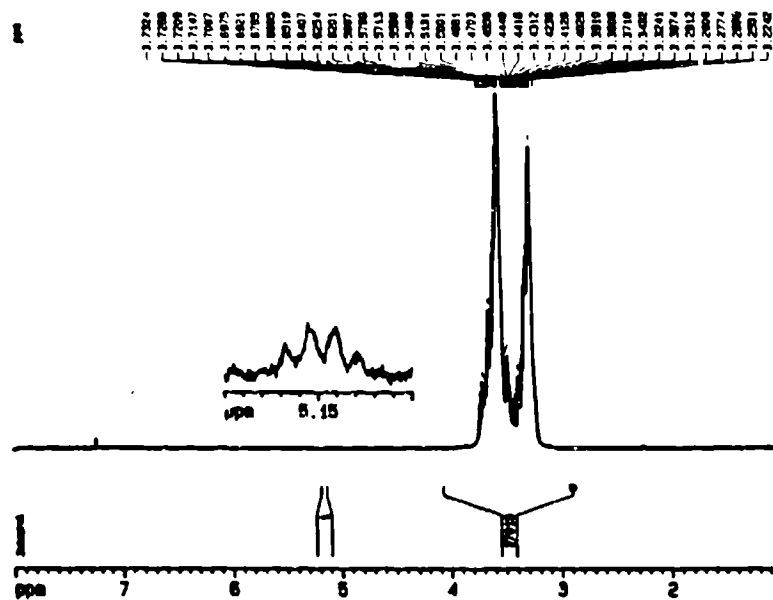


FIGURE 13. 400 MHZ. ^1H NMR Spectrum of GAP Azide Lot 200-2, Plus Excess TFAA.

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